

# Chapter 1

## CASTNet Overview

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*A national monitoring network was mandated as part of the 1990 Clean Air Act Amendments to determine the effectiveness of future emission reductions. The U.S. Environmental Protection Agency (EPA) established the Clean Air Status and Trends Network (CASTNet) to provide data to determine relationships between emissions, air quality, deposition, and ecological effects. The basic tenets of CASTNet are to define the spatial distribution of pollutants, detect and quantify trends in pollutants, implement monitoring in cooperation with other agencies and organizations, and implement monitoring to fill gaps in monitoring coverage. This report summarizes the CASTNet monitoring activities and the resulting concentration data for 1999.*

### Introduction

Atmospheric deposition takes place via two pathways: wet deposition and dry deposition. Wet deposition is the result of precipitation events (rain, snow, etc.) that remove particles and gases from the atmosphere. Dry deposition is the transfer of particles and gases to the landscape in the absence of precipitation. While wet deposition rates of acidic species across the United States have been well documented over the last 20 years, comparable information has been unavailable for dry deposition rates. However, CASTNet is now providing estimates of dry deposition at sites across the United States.

In 1986, EPA established the National Dry Deposition Network (NDDN). The objective of the NDDN was to obtain field data at approximately 50 sites throughout the United States to establish patterns and trends of dry deposition. The approach adopted by the NDDN was to estimate dry deposition using measured air pollutant concentrations and modeled deposition velocities estimated from meteorological, land use, and site characteristic data.

Passage of the Clean Air Act Amendments (CAAA) in 1990 required implementation of a national network to: 1) monitor the status and trends of air emissions, pollutant deposition, and air quality; 2) determine the effects of emissions on water quality, forests, and other sensitive ecosystems; and 3) assess the effectiveness of emission reduction requirements through operation of a long-term monitoring program. In response to the requirements of the CAAA, EPA, in coordination with the National Oceanic and Atmospheric Administration (NOAA), created CASTNet. CASTNet became operational in mid-1991, and the NDDN was incorporated into CASTNet at that time.

EPA contracted Environmental Science & Engineering, Inc. (ESE) to establish and operate CASTNet. The primary goals of CASTNet are to establish an effective monitoring and assessment network to determine the status and trends of air pollution levels and their environmental effects, and to develop a scientific database to improve understanding of sources and effects for policy considerations. In meeting these goals,

an important objective of CASTNet is to establish patterns and trends of dry deposition. As with the NDDN, CASTNet estimates dry deposition using measured air pollutant concentrations and deposition velocities ( $V_d$ ) estimated from meteorological, land use, and site characteristic data. The Multi-Layer Model (MLM), currently used for dry deposition flux simulations, has been described recently by Meyers *et al.* (1998) and Finkelstein *et al.* (2000). In 1999, CASTNet included measurements of ozone ( $O_3$ ) concentrations, aerosols, and visibility-related parameters.

The National Park Service (NPS) is responsible for the protection and enhancement of air quality related resources in national parks and wilderness areas. To carry out these responsibilities, NPS has developed an air quality program that involves a wide range of activities, including air quality monitoring and modeling, and participation in CASTNet. In 1994, under a partnership agreement with EPA, NPS merged 17 previously operating sites into the network and assumed operation of two other park sites. New sites have been added subsequently. In 1999, NPS operated 27 sites at various national parks and monuments, mostly in western locations. The NPS and EPA are responsible for operating their sites under a common set of quality assurance standards and similar monitoring and data validation protocols. The measurements from the NPS and EPA sites are merged into a single database and delivered to EPA quarterly.

This report summarizes results of CASTNet monitoring activities for 1999. Included in this summary are annual and quarterly mean concentration data for atmospheric sulfur and nitrogen species with a description of temporal variability; estimates of wet and dry deposition with an analysis of trends in concentrations and depositions;  $O_3$  data for 1999; concentrations of fine mass for 1999 with time series analysis from 1994 through 1999; and results from the Quality Assurance (QA) Program.

## Network Description

The status of CASTNet, as of December 1999, is shown in Figure 1-1. Seventy-nine sites were operational. Seventy-six of the 79 sites were equipped with filter packs for measurement of pollutant concentrations and estimation of deposition rates. Seventy-four sites measured  $O_3$ . Two dry deposition sites included collocated sampling systems for determining network precision. Appendix A provides the location and operational characteristics of each CASTNet site by state. This includes information on site location, start date, latitude, longitude, elevation, and the types of measurements taken at the site. Also included is information on the type of surrounding terrain and land use, a designation regarding the representativeness of each site with MLM modeling assumptions, and the sponsoring agency (EPA or NPS).

CASTNet included 8 sites that take visibility-related measurements, including aerosol filter packs. Six of these sites measured dry

deposition, and 2 sites also measured optical properties of the atmosphere. The Sikes, LA site (SIK570) had collocated equipment for quality assurance purposes. A collocated visibility system (nylon filters only) was installed at Quaker City, OH (QAK572) during August 1999.

In January 1999, all wet deposition monitoring activities were transferred to the National Atmospheric Deposition Program (NADP) under the National Trends Network (NTN) protocol to promote nationwide consistency in wet deposition monitoring. NADP/NTN assumed responsibilities for the administration of wet deposition activities at 15 sites, which included analysis and reporting of precipitation chemistry samples. These activities were previously carried out at 19 CASTNet sites to fill gaps in geographic coverage of NADP/NTN. In transferring activities to NADP/NTN, operations at three of the CASTNet wet deposition sites were discontinued because of their proximity to nearby NADP/NTN sites; and the collocated site at Scotia Range, Pennsylvania was terminated because collocation with NADP/NTN was no longer needed. More information about NADP/NTN may be found at their website: <http://nadp.sws.uiuc.edu>.

One of the CASTNet sites is located in Egbert, Ontario, Canada (EGB181). At this site, day and night samples are collected weekly, along with a standard weekly composite CASTNet filter pack. This set-up provides the means to compare results from CASTNet with the Canadian Air and Precipitation Monitoring Network (CAPMoN).  $O_3$  is not measured at EGB181.

Table 1-1 summarizes significant operational events and decisions for 1999. More details on the history of the network can be found in the CASTNet 1998 Annual Report (ESE, 1999a).

## Methods

This section provides a brief overview of methods employed for CASTNet. Step-by-step protocols and additional details on these activities can be found in the CASTNet Field Operations Manual, Laboratory Operations Manual, Draft Data Management Manual, and the Draft Quality Assurance Project Plan (QAPP) (ESE, 1990a, 1990b, 1998, 1999b).

### Field Operations

Ambient measurements for sulfur dioxide ( $SO_2$ ), particulate sulfate ( $SO_4^{2-}$ ), particulate nitrate ( $NO_3^-$ ), nitric acid ( $HNO_3$ ), particulate ammonium ( $NH_4^+$ ), continuous  $O_3$ , and meteorological variables required for dry deposition calculations were performed at each CASTNet site. Meteorological variables and  $O_3$  concentrations were recorded continuously and reported as hourly averages consisting of a minimum of 9 valid 5-minute averages. Atmospheric sampling for sulfur and nitrogen species was integrated over weekly collection periods using a three-stage filter pack (Figure 1-2). In this approach, particles

**Figure 1-1.** Locations of CASTNet Sites as of December 1999

**Table 1-1. Significant Operational Events During 1999**

<b>January 1999</b>	<p>Major fire on the ESE Gainesville campus destroyed the CASTNet calibration lab, spare parts storage, staging, shipping and receiving, and the mobile dry deposition system.</p> <p>Filter concentration (dry deposition) began at CDZ171/571 and QAK172/572.</p> <p>All visibility Teflo® filters were converted (“mask” removed) from a 25 mm deposit surface to a 37 mm deposit surface.</p> <p>Operation of the CASTNet precipitation chemistry (wet deposition) sites was transferred to NADP/NTN.</p>
<b>March 1999</b>	<p>ESE lab switched to vendor-supplied control and calibration standards, rather than using standards produced in-house.</p>
<b>April 1999</b>	<p>Completed construction of new calibration lab.</p> <p>Analytical chemistry lab moved into new facilities.</p>
<b>June 1999</b>	<p>Revised Draft Quality Assurance Project Plan (QAPP).</p>
<b>July 1999</b>	<p>Initiated interlaboratory comparison studies with CAPMoN.</p> <p>Provided wet deposition sampling equipment to the St. Regis Mohawk Tribe in New York and the Penobscot Nation in Maine.</p>
<b>August 1999</b>	<p>Initiated collocated denuder/nylon sampling at QAK572 on a 6-day schedule.</p>
<b>September 1999</b>	<p>Hired a new QA Supervisor.</p> <p>Initiated a new NPS site in Hawaii.</p>
<b>December 1999</b>	<p>All CASTNet equipment was deemed Y2K compliant.</p>

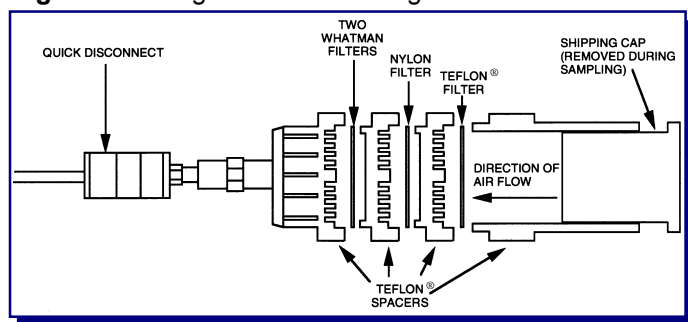
and selected gases were collected by passing air at a controlled flow rate through a sequence of Teflon®, nylon, and Whatman filters. The Teflon® filter removed particulate  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$ , and the nylon filter removed  $\text{HNO}_3$ . The Whatman filter, a cellulose fiber base impregnated with potassium carbonate ( $\text{K}_2\text{CO}_3$ ), removed  $\text{SO}_2$ . Two Whatman filters (Figure 1-2) were used. In practice, a fraction (usually <20%) of ambient  $\text{SO}_2$  is captured on the nylon filter. The nylon filter  $\text{SO}_2$  and Whatman filters  $\text{SO}_2$  were summed to provide weekly average concentrations. The nylon filter  $\text{HNO}_3$  was converted to  $\text{NO}_3^-$  and added to the  $\text{NO}_3^-$  collected on the Teflon® filter to provide weekly total  $\text{NO}_3^-$  concentrations.

Filter packs were prepared and shipped to the field weekly and exchanged at each site every Tuesday. Blank filter packs (i.e., trip blanks) were collected quarterly to evaluate contamination during shipment and handling. At 15 sites, wet deposition samples were collected weekly by NADP/NTN and shipped to the NADP/NTN lab for chemical analysis.

Filter pack sampling and  $\text{O}_3$  measurements were performed at 10 meters (m) using a tilt-down aluminum tower (Aluma Tower, Inc.). Filter pack flow was maintained at 1.50 liters per minute (Lpm) at eastern sites and 3.00 Lpm at western sites, for standard conditions of 25 degrees Celsius ( $^{\circ}\text{C}$ ) and 760 millimeters of mercury (mm Hg) with a mass flow controller (MFC).

The CASTNet continuous measurements are archived as hourly averages and are indexed at the end of each hour (i.e., hour 2300 references the measurement over the hour 2200 through 2300). The discrete filter data are archived as weekly averages and are referenced by start date and time. CASTNet generally uses a 75% data completeness criterion to constitute a valid sample, e.g., 75% of possible hourly flow values are required to constitute a valid weekly average concentration from an exposed filter. An exception to the 75% requirement is the calculation of quarterly mean concentrations and fluxes where 8 or more valid weekly values of 13 possible values are acceptable. Procedures to aggregate weekly data to obtain quarterly and annual measurements are discussed in Chapter 2. See Chapter 7 for data completeness requirements.

Ambient  $\text{O}_3$  concentrations were measured via ultraviolet (UV) absorbance with a Thermo-Environmental Model 49-103 analyzer. Zero, precision [60 parts per billion (ppb)], and span (400 ppb) checks of the  $\text{O}_3$  analyzer were performed every Sunday using an internal  $\text{O}_3$  generator. Although precision and accuracy for CASTNet  $\text{O}_3$  data (see Chapter 7) meet data quality objectives, CASTNet quality assurance procedures for the EPA  $\text{O}_3$  analyzers do not strictly conform to the EPA requirements for State and Local Monitoring Stations (SLAMS) monitoring as described in 40 Code of Federal Regulations (CFR) Part 58, Appendix A (EPA, 1998c). On the other hand, the NPS analyzers meet all requirements.

**Figure 1-2. Diagram of Three-Stage Filter Pack**

In addition, various observations were periodically made at CASTNet sites to support model calculations of dry deposition. Site operators recorded surface conditions (e.g., dew, frost, snow) and vegetation status weekly. Vegetation status and land-use information were used to define the distribution and condition of plant species around each site that could influence deposition rates for gases and particles. Vegetation data were obtained to track evolution of the dominant plant canopy, from leaf emergence (or germination) to senescence (or harvesting).

Leaf area index (LAI) measurements were taken at all CASTNet sites during the summers of 1991 and 1992, and at most of the NPS sites during the summer of 1997. LAI is the one-sided leaf area of the plant canopy per unit area of ground at full leaf emergence and has been shown to play an important role in atmosphere-canopy exchange processes (McMillen, 1990). LAI was measured using an LAI-2000 Plant Canopy Analyzer manufactured by Li-Cor, Inc. (Li-Cor) (Lincoln, NE). The LAI-2000 makes indirect (i.e., non-destructive) estimates of LAI from simultaneous measurements of light interception by the plant canopy at five angles of inclination (Li-Cor, 1989).

All field equipment was subjected to semiannual inspections and multipoint calibrations using standards traceable to the National Institute of Standards and Technology (NIST). Results of field calibrations were used to assess sensor accuracy and flag, adjust, or invalidate field data. In addition, audits were performed annually by Air Resource Specialists, Inc. (ARS). Results of 1999 QA activities are discussed in Chapter 7.

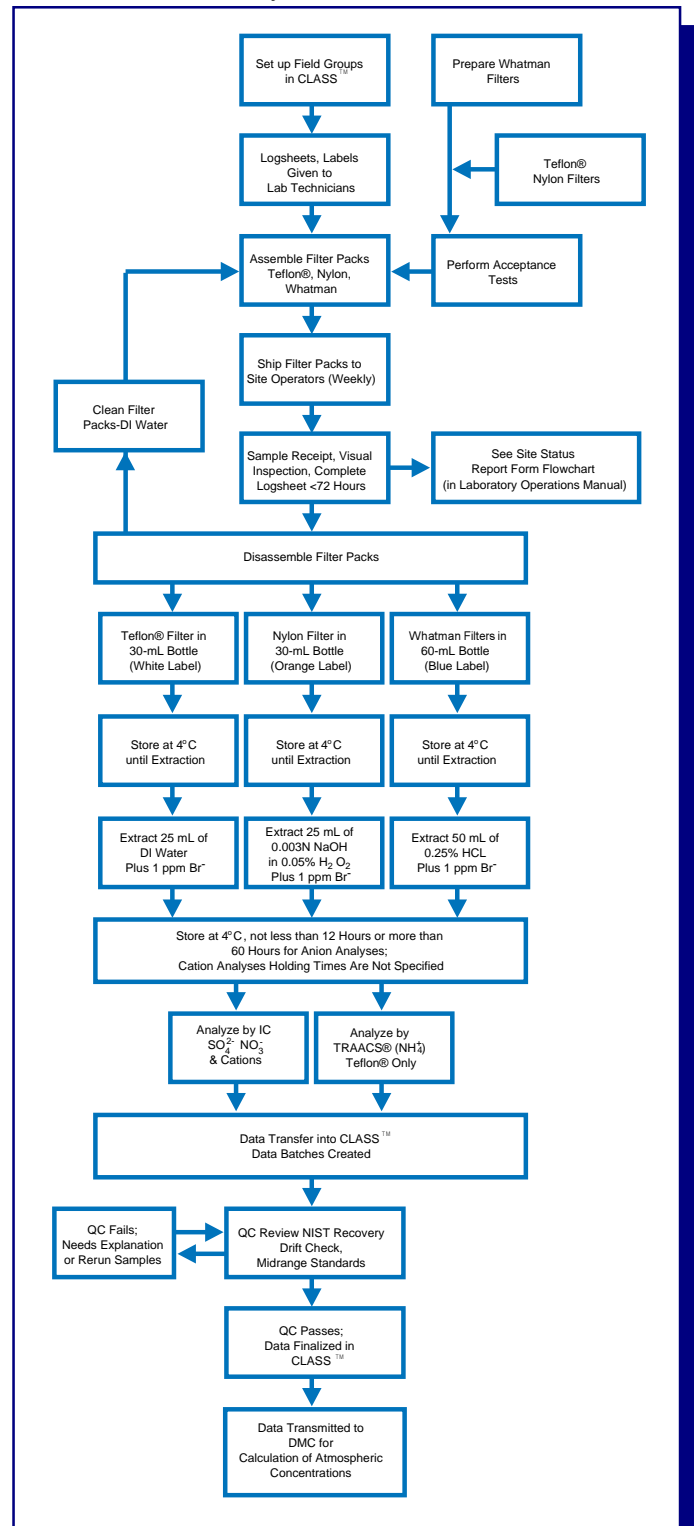
### Laboratory Operations

Filter pack samples were loaded, shipped, received, extracted, and analyzed by ESE personnel at the Gainesville, Florida laboratory. Filter packs contained three types of filters in sequence: a Teflon® filter for collection of aerosols, a nylon filter for collection of  $\text{HNO}_3$ , and dual  $\text{K}_2\text{CO}_3$ -impregnated cellulose filters for collection of  $\text{SO}_2$ .

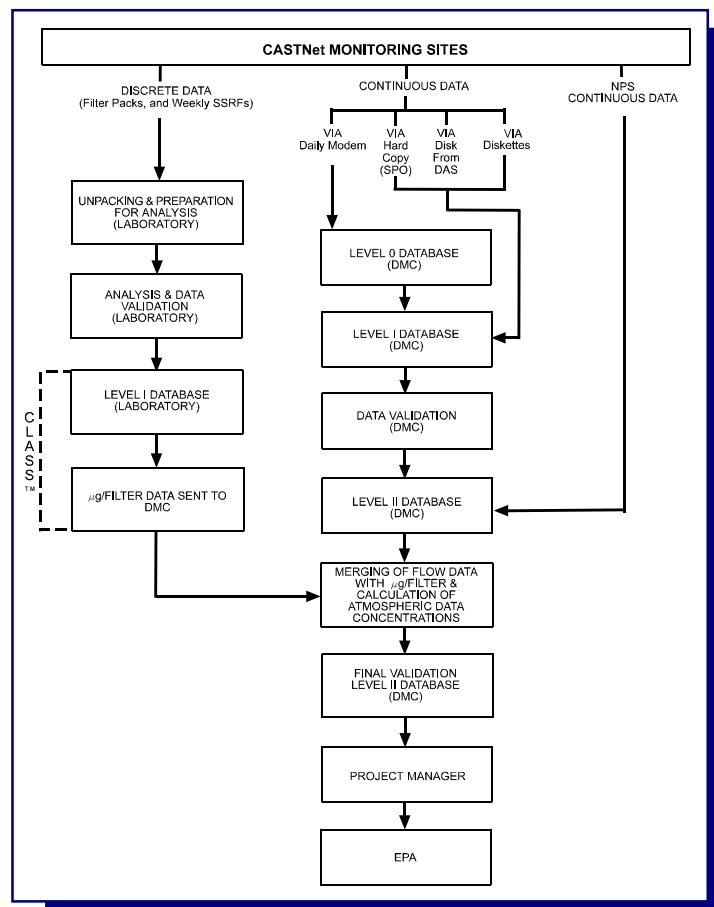
Following receipt from the field, exposed filters and blanks were extracted and then analyzed for  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  by micromembrane-suppressed ion chromatography (IC). Teflon® filter extracts were also analyzed for  $\text{NH}_4^+$  by the automated indophenol method using a TRAACS-800 Autoanalyzer system. All analyses were completed within 72 hours of filter extraction. Figure 1-3 depicts the sequence of laboratory operations for filter pack sample analyses.

Results of all valid analyses were stored in the laboratory data management system [Chemistry Laboratory Analysis and Scheduling System (CLASS™)]. Atmospheric concentrations were calculated (based on volume of air sampled) following validation of hourly flow data.

**Figure 1-3. Flowchart of Laboratory Operations for Filter Pack Analyses**





**Figure 1-4. Flow of Data Through CASTNet Data Management System**

### Data Management

This section summarizes the overall data management system used for CASTNet. The flow of data is shown in Figure 1-4.

#### Field Data

Field data, or continuous data, were handled by the Data Management Center (DMC). The DMC activities consisted of five major operations: data acquisition, data validation, data management, model operation, and transmittal to EPA. These activities are described briefly in this subsection. Details on data management and operation of the MLM are provided in the Draft CASTNet Data Management Manual (ESE, 1998), and the Draft QAPP (ESE, 1999b). The MLM is discussed later in this section.

The data acquisition process stresses multiple levels of redundancy to minimize data loss. The primary mode of data acquisition from the field was via telephone modem. The sites were automatically polled daily using an IBM-compatible PC and software developed by Odessa Engineering, Inc. (Odessa Engineering). The polling software enables recovery of hourly data and status files, power failure logs, and automated calibration results from the previous 7 days. The program also maintains synchronization of

the network by checking the clock within each data acquisition system (DAS) and correcting the time if it deviates from expectation by more than 3 minutes. If daily polling resulted in incomplete data capture from any site, then diskettes of data from the primary and backup DAS were read into the database management system. If data were still incomplete, the missing data were entered manually either from site printouts (SPO) or recovered from data cartridges.

The CASTNet database management system consists of several components. The first is a custom version of Odessa Engineering's Environmental Aide software. The Environmental Aide system consists of two programs, ENVICOM and ENVAID, which reside on a Local Area Network (LAN) in the DMC. ENVICOM is a communications and data transmittal package which polls each site daily and incorporates the previous day's hourly averages into the raw database. Data retrieved through ENVICOM were entered directly into the raw database and stored in binary data and status files. ENVAID was used previously to store the binary data and to validate the continuous measurements. In 1999, ENVAID was used only to help validate the flow data from the eight visibility sites. The CASTNet data are now managed and archived using Microsoft® (MS) SQL Server™, a relational database management system (RDBMS). The binary data are stored in SQL Server™.

After daily polling of all stations, Level I validation procedures were initiated. Daily summaries were generated as data were collected from the sites. Field operations personnel then reviewed these reports daily to detect potential problems with minimal delay. Site Status Report Forms (SSRF) and operator logsheets were reviewed weekly to verify the validity of the data received. Problems identified by the field operations personnel were entered into a Field Problem Data database for subsequent use by the data validators.

The purpose of Level I validation is to develop a complete database. The process involves generating reports to establish data completeness and define periods of missing data. The process continues by recovering missing data from (1) the disk containing data from the primary cartridge, (2) data from the backup cartridge, and/or (3) data from SPO. Level I validation ends when the data completeness is maximized and all time periods and sources of missing data are documented.

Level II validation involves a more detailed screening of the data. SSRF, operator logsheets, calibration data, and audit results are reviewed for each site. In addition, data are screened using an automated program, which identifies potential problems such as values greater than the expected range and invalid combinations of status flags, values, and spikes. All review and editing activities are documented.

When all documentation was reviewed and the database was edited to the satisfaction of the Data Operations Manager, approximately 10% of the database was audited for traceability. Upon completion of the QA review, the database was verified as Level II.

All NPS continuous O<sub>3</sub> and meteorological data were received from ARS at Level II.

Again, the CASTNet data are managed using a MS SQL Server™ based RDBMS. Table 1-2 provides a list of tables that constitute the database.

### Laboratory Data

Data generated from filter pack samplers (discrete data) were managed by CLASS™. Figure 1-5 depicts the flow of data management activities in CLASS™.

Attainment of Level I validation for discrete data consisted of meeting the following criteria:

1. Data were determined to be reasonable based on the analyst's evaluation of the data batch Quality Control (QC) sample results.
2. Data transfer by electronic or manual entry into CLASS™ were completed properly as evaluated by the Laboratory Operations Manager.
3. The appropriate analytical batches were processed through an automated QC checking routine performed by CLASS™ and determined to be acceptable. For each analytical batch, a data flag was generated if any of the following occurred:
  - a. Insufficient QC data were run for the batch.
  - b. Correlation coefficient of standard curve was less than 0.995.
  - c. The 95% confidence limit of the Y-intercept exceeded the limit of quantification.
  - d. Sample response exceeded the maximum standard response in the standard curve (i.e., the sample must be diluted to bring the response within the range of the curve).
  - e. Continuing verification samples (CVS) exceeded the recovery limits.
  - f. Reference samples exceeded accuracy acceptance limit.

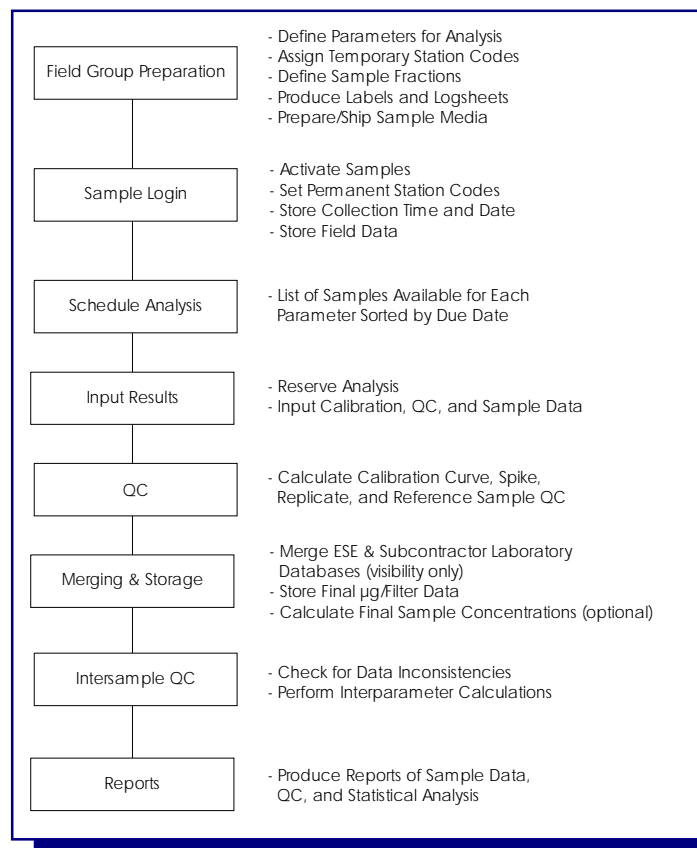
A batch with one (or more) flags was accepted only if written justification was provided by the Laboratory Operations Manager.

To calculate atmospheric concentrations from filter pack samples, filter pack flow data were merged with laboratory data at the DMC. Atmospheric concentrations were calculated only if valid hourly averages for filter pack flow represented at least 75% of the sampling period and analytical data met all QC criteria. Filter pack samples with greater than 75% but less than 90% valid flow data were flagged to indicate uncertainty in concentration calculations.

Attainment of Level II validation required that:

1. All Level I data meeting QC criteria were reviewed and evaluated as acceptable by the Laboratory Operations Manager.
2. A review and evaluation of any data flags was completed by the Laboratory Operations Manager.
3. Written justification for acceptance of data that did not meet QC criteria was approved by the QA Supervisor.

**Figure 1-5. Flowchart of CLASS™ Program**



4. The filter mass was provided to the DMC for calculating final filter pack concentrations.

After the DMC produced a set of filter concentrations, CASTNet scientists reviewed the data. The concentrations were reviewed for consistency among analytes from the three filters for a specific week and also from week-to-week for a specific site. Concentration values were compared to regional and historical data for reasonableness. On/off dates and times and comment codes were reviewed to help determine the validity of the concentration values.

Based on this review, a scientist either invalidated suspect concentrations or requested a rerun of the chemical analysis of the filters. The rerun results were compared to the initial results and final concentrations were selected.

Level II concentration data were archived in the CASTNet MS SQL Server™ RDBMS (Table 1-2).

**Table 1-2.** Tables Currently in the SQL Server™ CASTNet Database

Table Name	Description
codes	Lists all QA codes, qualifiers, and status flags for each table in the database.
drychem	Ambient concentrations of gases and particles as measured by filter packs.
drychem_daynight	Day/Night ambient concentrations of gases and particles as measured by filter packs.
filter_pack	Dry chemistry filter pack data. Data input from SSRF.
formats	Data definitions for tables in the CASTNet data repository.
lab_comments	Laboratory comment codes associated with each filter pack.
labdata	Laboratory analytical and QC data in total micrograms.
leaf_angle	Leaf angle data used as input to create the lang.sph file. Used by MLM model.
leaf_status	Leaf status of site location as documented by the site operator during weekly site visit. Data input from SSRF.
metdata	Level II validated continuous meteorological data.
ozone	Level II validated continuous ozone data.
ozone_qc	Ozone autocalibration data.
plant	Plant types and coefficients. Used by MLM model.
plant_profile	Canopy data used as input to create the padprof1.20, padprof2.20, and padprof3.20 files. Used by MLM model.
site_plant_detail	Plant leaf out periods for each site. Used by MLM model.
site_plant_summary	Plant coverage for each site. Used by MLM model.
sites	CASTNet data collection sites information.
table_desc	Description of tables in the CASTNet data repository.
velan	Archived annual deposition estimates of concentration, deposition velocities, and fluxes aggregated from VELQR.
velhr	Archived MLM output providing hourly estimates for concentration, deposition velocity, and flux.
velqr	Archived quarterly deposition estimates of concentration, deposition velocities, and fluxes aggregated from VELWK.
velwk	Archived weekly deposition estimates of concentration, deposition velocities, and fluxes aggregated from VELHR for sequential Tuesday-to-Tuesday weeks.
vischem	Chemical speciation data from aerosol filter packs.
visflow	Hourly flow data for aerosol filter packs.
visneph	Nephelometer data (conforms to IMPROVE network standards).
wetdep	Wet deposition data.

### Multi-Layer Model

The original network design was based on the assumption that dry deposition or flux could be estimated as the linear product of ambient concentration ( $C$ ) and deposition velocity ( $V_d$ ):

$$\text{Flux} = \overline{C} \times \overline{V_d}$$

where the overbars indicate an average over a suitable time period (Chamberlain and Chadwick, 1953).

The influence of meteorological conditions, vegetation, and chemistry is simulated by  $V_d$ . Dry deposition processes are modeled as resistances to deposition (Meyers *et al.*, 1998):

$$R = R_a + R_b + R_c = 1/V_d$$

$R_a$ , the aerodynamic resistance, is inversely proportional to the atmosphere's ability to transfer material downward from the planetary boundary layer to the surface layer by turbulent processes.  $R_b$  is the boundary layer resistance to vertical transport (molecular diffusion) through a shallow (approximately 1 millimeter) nonturbulent layer of air in direct contact with the surface.  $R_b$  depends on the aerodynamics of the surface and the diffusivity of the pollutant being deposited.  $R_c$ , the canopy or surface uptake resistance, contains several terms (represented as parallel resistances) that account for the direct uptake/absorption of the pollutant by leaves, soil, other biological receptors within and below the canopy, and other surfaces such as rock and water.  $R_c$  contains parameterizations for vegetation type and density, solar radiation penetration of the canopy and wetness of the surface.  $R_c$  is difficult to treat theoretically, and the system of equations for estimating  $R_c$  is normally empirically adjusted based on direct observation of dry fluxes.



Using this physical and mathematical framework, two dry deposition models, Big Leaf and MLM, have been used to calculate dry deposition for CASTNet. Both models were developed by the NOAA Atmospheric Transport and Diffusion Division, Oak Ridge, TN. The Big Leaf model treats the vegetation canopy as a one-dimensional surface. Big Leaf model results, aggregated to seasonal and annual averages for 1991, have been reported by Clarke and Edgerton (1993).

The MLM is a variation of the Big Leaf model wherein similar calculations are applied through a 20-m layer canopy in which model parameters are modified by the redistribution of heat, momentum, and pollutants. The MLM requires the following input data: wind speed, wind direction, sigma theta, temperature, relative humidity, solar radiation, surface wetness, LAI, vegetative species and percent green leaf-out. The MLM also accounts for water and temperature stress, stomatal resistances of the vegetation, and deposition to snow surfaces. Additionally, several parameters (e.g., soil resistance) have been modified in the MLM from those used in the Big Leaf model. Dry deposition calculations for the CASTNet sites are currently made using a version of the MLM updated in 1998 and 2000.

The MLM was applied previously to simulate weekly depositions for the period 1987 to 1995. The results were reported in the CASTNet Deposition Summary Report (EPA, 1998a). Since then, a few changes have been made to the model. The current model simulates variable soil moisture. The algorithm for the soil uptake resistance has been changed to account for the presence of snow or for the presence of certain crops and grasses. The minimum wind speed was changed from 0.2 to 0.1 meters per second (m/sec) and, if the relative humidity is above 89%, the surface wetness is set to 1.0.

A change in modeling procedures was implemented for the MLM results reported herein. The algorithm for the soil uptake resistance was applied continuously for all hours at a CASTNet site with valid meteorological input data, regardless of the availability of concentration data. Previously, the algorithm was not applied for weeks with missing concentration data.

The MLM software code was updated according to established version control procedures (ESE, 2001). The most recent software designated as Version 2.1 represents a significant improvement over earlier versions. The update includes changes in the application of the algorithm for soil resistance mentioned above. The application of the soil resistance method is now done continuously, regardless of whether concentration data are available for a time period. Through these changes,  $V_d$  values are calculated for every hour and values of soil moisture are not reinitialized when concentration data are missing. This eliminates discontinuities in the evolution of the deposition velocities. Also, weekly fluxes are calculated properly for each week from Tuesday at 0800 to the following Tuesday at 0800. Appendix B

provides data on the differences in hourly  $V_d$  for MLM Versions 2.0 and 2.1.

The meteorological variables used to determine  $R_a$  and  $R_b$  were obtained from the 10-m meteorological tower at each of the sites, normally located in a clearing over grass or another low vegetative surface. Data on vegetative species and percent green leafout were obtained from site surveys and observations by the site operator. LAI measurements were taken during 1991, 1992 and 1997 at times of summer maximum leafout. LAI values that are used in the MLM were extrapolated from these measurements using percent leafout observations. The resistance terms ( $R_a$ ,  $R_b$ , and  $R_c$ ) were calculated for each chemical species and major vegetation/surface type every hour. The  $V_d$  for a site was then calculated as the area-weighted  $V_d$  over vegetation types within 1.0 kilometer (km) of the site. Hourly  $V_d$  values and weekly integrated concentrations were used to produce hourly fluxes of  $\text{HNO}_3$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and  $\text{SO}_2$ .  $\text{O}_3$  flux was calculated using hourly  $\text{O}_3$  measurements and hourly  $V_d$  values. Weekly flux calculations were considered valid if more than 75% of hourly  $V_d$  values were available for that week. Weekly values were aggregated to quarterly averages if 8 weeks in a quarter were valid. Quarterly averages were aggregated to annual only if three quarters were valid.

Results of deposition simulations for the period 1990 through 1999 are presented in Chapter 3.

### Data Delivery

Quarterly reports and data were submitted to EPA in ASCII format (MySQL™ insert statements or comma delimited) on a CD-ROM along with a hardcopy. Also provided to EPA were QC reports listing parameter averages by site and aggregated counts of status flags. Quarterly reports summarized network activities in the period and presented results of all field and laboratory QC checks. The quarterly reports included maps of filter concentration data and aerosol data (including reconstructed fine mass). Trends analysis and time series plots were presented.  $\text{O}_3$  concentrations were presented in terms of 1-hour and 8-hour concentrations.

### PM<sub>2.5</sub> Aerosol/Visibility Network

Visibility monitoring includes three measurement types as defined by the IMPROVE program:

- Aerosol–Aerosol characteristics (concentration, composition, and size) are determined to relate atmospheric optical properties with various species.
- Optical–Optical properties (e.g., light scattering) of the atmosphere are monitored for a scene-independent measure of air quality.
- Scene–Visual characteristics (e.g., through photos) of a scene are monitored to document scene-specific visibility.

IMPROVE protocols were used to guide the CASTNet monitoring, instrument specifications, siting criteria, sample frequency, quality assurance, and analytical techniques.

The 1999 CASTNet Visibility Network consisted of eight sites in the eastern United States spanning from Louisiana to Illinois to New York (Figure 1-6). The locations of the visibility sites are listed in Appendix A. The visibility sites have been operating since October 1993.

Of the three measurement types, aerosol and light scattering measurements were taken during the 1999 sampling season (see Appendix A). Photographs were not taken during 1999. All eight sites collected aerosol samples, and two sites measured atmospheric light scattering. Aerosol sampling was conducted using time-integrated systems where 24-hour samples were collected every six days. Each aerosol sampling system consisted of three separate single-stage filter packs designated as denuder/nylon, Teflo®, and quartz (Figure 1-7). These designations refer to the type of filter media deployed in the respective filter pack.

The aerosol sampling system included independent flow channels for each of the three filter packs: two were operated at 10 Lpm, and one at 16.7 Lpm. All were equipped with MFC and located in a weather-proof enclosure at 10-m above ground level. The channel for  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  was operated at 10 Lpm and included a 2.5-micrometer ( $\mu\text{m}$ ) cyclone, followed by a single base-impregnated (sodium carbonate) annular denuder tube and a single-stage nylon filter pack. The nylon filter was 47 millimeters (mm) in diameter. The trace/crustal elements and carbon channels included a 2.5- $\mu\text{m}$  cyclone followed by a single-stage filter pack. Trace/crustal element samples and mass were collected on Teflo® filters (37 mm diameter). The Teflo® filter pack flowrate was 16.7 Lpm. Carbon samples were collected on precombusted quartz fiber filters (37 mm diameter) at 10 Lpm.

As part of optical monitoring, nephelometers were used to measure atmospheric light scattering at two sites: Cadiz, KY (CDZ571) and Quaker City, OH (QAK572).

## Methods

### Laboratory Operations

After every third sampling event, the denuders, nylon, Teflo®, and quartz filters were shipped to the ESE laboratory from each visibility site. Each month, the ESE laboratory shipped valid Teflo® and quartz samples to Chester LabNet and Sunset Laboratory, Inc. (Sunset Laboratory), respectively.

**Figure 1-6.** Locations of CASTNet Visibility Monitoring Sites

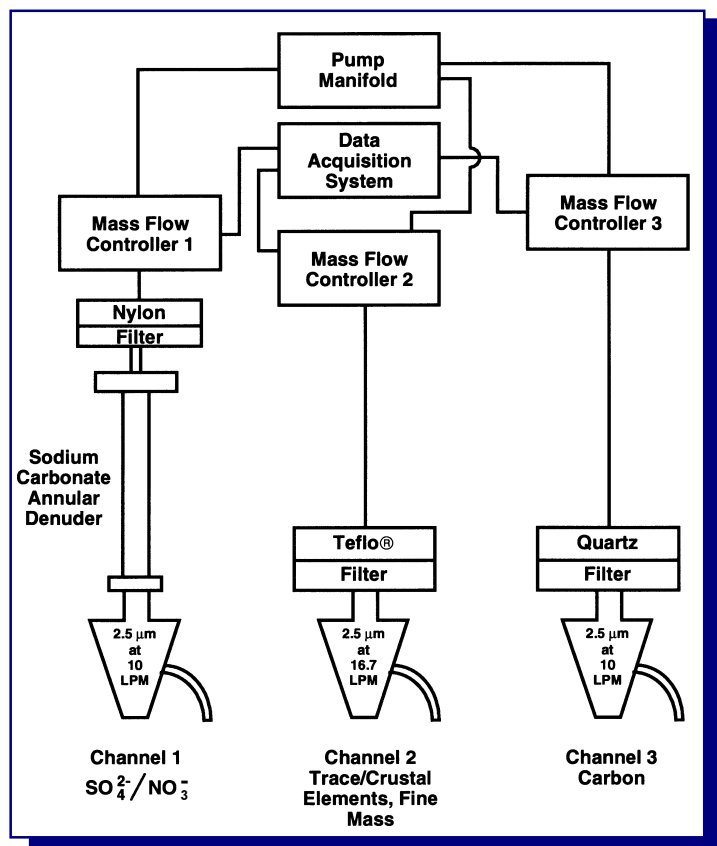


The ESE laboratory extracted the nylon filters, and then the nylon extracts were analyzed for  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  by IC.

Teflo® filters were analyzed by Chester LabNet for mass (gravimetry) and the elements sodium ( $\text{Na}^+$ ) through lead (Pb) by X-ray fluorescence (XRF). The analysis of elements by XRF uses a Kevex Model 771 spectrometer with electronic and computer software upgrades.

Quartz filters were analyzed by Sunset Laboratory for elemental and organic carbon using thermal-optical analysis (TOA). The TOA method is based on the principle that organic and elemental carbon react under different temperature and oxidation conditions.

Generally, mass was determined by following protocols (e.g., filter equilibration) based on 40 CFR 50, Appendix L (EPA, 1998d). Filters were acceptance-tested in a laminar flow hood and tare-weighted on a Cahn Model 31 microbalance under computer control. Tare-weighted filters are shipped to the field in individual plastic petri slides with snap lids. After exposure in the field, filters are gross weighted on the same balance, and deposit net weights are calculated from the difference in the gross and tare weights. All gravimetry operations are performed in a temperature- $(21 \pm 3^\circ\text{C})$  and humidity- $(40 \pm 5\%$  relative humidity) controlled environment.

**Figure 1-7.** Aerosol Sampling System

### *Data Management*

Visibility data were managed cooperatively by ESE and ARS. Continuous field data from nephelometers and temperature and relative humidity sensors were acquired by the ESE DMC and relayed to ARS daily. ESE validated aerosol data, and ARS validated  $b_{\text{scat}}$  data. Following validation, all  $b_{\text{scat}}$  data and associated documentation were transferred to the CASTNet DMC at ESE. Data were delivered to EPA quarterly.

